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Preparation of carbon supported Pt–P catalysts and its electrocatalytic performance for oxygen reduction

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ABSTRACT

The carbon supported PtP (PtP/C) catalysts were synthesized from Pt(NO_3)$_2$ and phosphorus yellow at the room temperature. The content of P in the PtP/C catalysts prepared with this method is high and the average size of the PtP particles is decreased with increasing the content of P. The electrocatalytic performances of the PtP/C catalysts prepared with this method for the oxygen reduction reaction (ORR) are better than that of the commercial Pt/C catalyst. The promotion action of P for enhancing the electrocatalytic performance of the PtP/C catalyst for ORR is mainly due to that Pt and P form the alloy and then the electron density of Pt is decreased.

1. Introduction

The proton exchange membrane fuel cell (PEMFC) has the good potential applications as the power sources for transportation and stationary applications. However, the commercialization of PEMFC is still hindered by several factors, such as the poor kinetics of the cathodic reaction. The Pt/C catalyst is usually used as the cathodic catalyst in PEMFC. In order to improve the electrocatalytic performance of the Pt/C catalyst for ORR, many Pt-based composite catalysts have been widely investigated. The most investigated Pt-based catalysts are composite catalysts of Pt and other metal elements, such as PtV [1], PtCr [2], PtTi [3], PtFe [4,5], PtCo [4,6], PtNi [4,7], PtCu [8], PtGa [9], PtRu [10,11], PtPd [12,13], PtCrCu [14], PtCrCo [15], PTFeNi [16], Pt-metal oxide [17] and Pt-macrocycle compound catalysts [18–20]. Only few composite cathodic catalysts of Pt and non-metal catalyst, such as PtP catalyst have been reported [21,22].

In the previous reports, the PtP/C catalysts were prepared with the self-redox method of Na_2HPO_2 or H_3PO_2 and their electrocatalytic performances for ORR are better than that of Pt/C catalyst. However, the content of P in the catalysts prepared with the self-redox method of Na_2HPO_2 or H_3PO_2 is small. For example, the weight ratio of Pt and P in the PtP/C catalyst prepared with the self-redox method of H_3PO_2 is only is only 1.0:0.1 [21]. In this study, the PtP/C catalyst was prepared from Pt(NO3)$_2$ and phosphorus yellow at the room temperature. The content of P in the PtP/C catalyst prepared with this method is high. Therefore, its electrocatalytic performance for ORR is high.

2. Materials and methods

2.1. Preparation and characterization of PtP/C catalysts

The preparation procedure of the PtP/C catalyst is as follows. After 60 mg Vulcan XC-72 carbon, certain volume of the anhydrous ethanol and phosphorus yellow were mixed with stirring for 1 h at 20 ± 2 °C. Then, certain amount of Pt(NO_3)$_2$ in anhydrous ethanol was added into the above suspension at stirring. One hour later, 100 mg $NaBH_4$ in 10 mL water was added into the suspension with stirring for 2 h. Finally, the suspension was filtered, washed and dried in a vacuum oven at 60 °C. The PtP/C catalyst with 20 wt.% Pt was obtained. According to the atomic ratios (8:1, 4:1, 2:1, 1:1, 1:2) of Pt and P, the PtP/C catalysts obtained were noted as the Pt_8P_1/C, Pt_4P_1/C, Pt_2P_1/C, Pt_1P_1/C and Pt_1P_2/C catalysts, respectively. For comparison, the Pt/C catalyst with 20 wt.% Pt from JM Co. was used.

The X-ray diffraction (XRD) measurements of the PtP/C catalysts were carried out on Model D/max-r C diffractometer using Cu–Ka radiation (k = 0.15406 nm) operating at 45 kV and 100 mA. The average particle size and morphology of the PtP/C catalysts were evaluated using the transmission electron microscopy (TEM) on Tecnai G2205-TWTN (FET) instrument operating at 200 kV. The

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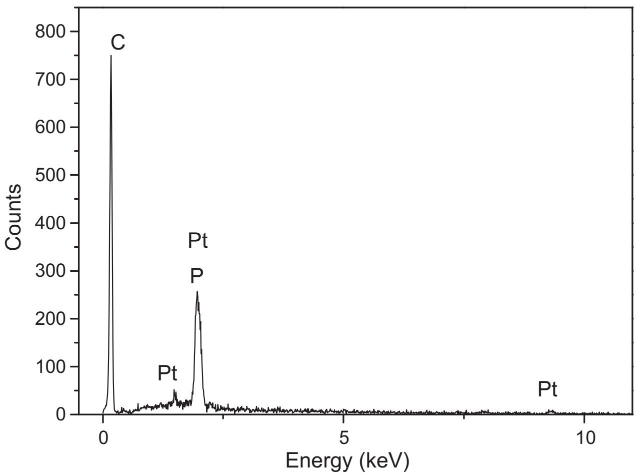

Fig. 1. EDX spectrum of the Pt_1P_1/C catalyst.

catalyst composition was determined with energy dispersive X-ray (EDX) analysis system of (GENESIs2000 XMSX, USA, EDAX).

2.2. Electrochemical measurements

The electrochemical measurements were performed using a CHI potentiostat/galvanostat and a conventional three-electrode electrochemical cell. The counter electrode was a Pt plate. The Ag/AgCl electrode was used as the reference electrode and all potentials were quoted with respect to the Ag/AgCl electrode. The glass carbon electrode with 3 mm diameter was used as the substrate of the working electrode.

The working electrode was prepared as follows. 10 mg PtP/C catalyst, 0.33 mL Nafion solution (5 wt.%, Aldrich), 0.83 mL ethanol and 0.83 mL water were mixed ultrasonically to obtain the catalyst slurry. 2.8 μL slurry was spread on the surface of the glassy carbon electrode. After drying, the working electrode was obtained. The electrode surface contains about 40 $\mu g\,cm^{-2}$ Pt–P. The electrolyte is 0.5 M H_2SO_4. The electrocatalytic performance of the catalyst for ORR was measured with the rotating disk electrode. Before the electrochemical measurement, the high-purity oxygen was bubbled into the solution for 20 min. All the electrochemical measurements were carried out at 30 ± 1 °C.

3. Results

3.1. Structure characterization of catalysts

Fig. 1 shows the EDX spectrum of the Pt_1P_1/C catalyst. The Pt and P peaks were observed in Fig. 1. It has been calculated that the PtP/C catalyst contains about 18.8 wt.% Pt, illustrating that $Pt(NO3)_2$ is almost completely reduced The weight ratio of Pt and P in the Pt_1P_1/C catalyst calculated from Fig. 1 is 20.52:5.12, indicating that the content of P in the PtP/C catalyst is high.

Fig. 2 displays the XRD patterns of the PtP/C catalysts and the Pt/C catalyst. In the XRD pattern of the Pt/C catalyst (Fig. 2, Curve f), the diffraction peak at $2\theta = 24.7^\circ$ is due to the C(0 0 2) crystal face. Other diffraction peaks are located around 39.8°, 46.6°, 67.8° and 81.1°, respectively. They are corresponding to the 2θ values of the characteristic diffraction peaks of Pt(1 1 1), (2 0 0), (2 2 0) and (3 1 1) crystal faces of the face centered cubic crystallinity, respectively, illustrating that the Pt particles in the Pt/C catalyst possess the face centered cubic crystal structure (JCPDS card: 04-802). The 2θ values of the diffraction peaks of the PtP particles in the PtP/C catalysts are slightly larger than the corresponding 2θ values of the diffraction peaks of the Pt particles in the Pt/C catalyst. The average size of the PtP and Pt particles can be calculated with the method reported in the literatures [23,24]. The average sizes of the PtP particles in the Pt_8P_1/C, Pt_4P_1/C, Pt_2P_1/C, Pt_1P_1/C and Pt_1P_2/C catalysts are 5.5, 4.6, 4.3, 3.1 and 1.1 nm, respectively. The average size of the Pt particles in the Pt/C catalyst is 2.8 nm.

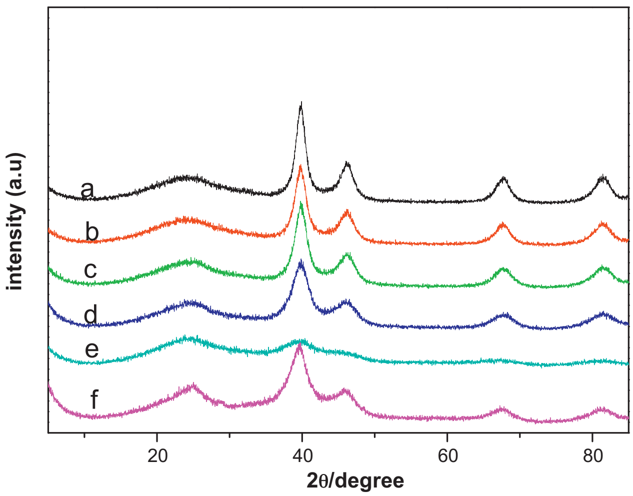

Fig. 2. XRD patterns of (a) Pt_8P_1/C, (b) Pt_4P_1/C, (c) Pt_2P_1/C, (d) Pt_1P_1/C, (e) Pt_1P_2/C and (f) Pt/C catalysts.

Fig. 3 represents the TEM images of Pt/C and Pt_1P_1/C catalyst. After measuring more than 100 nanoparticles randomly from TEM images of Pt/C and Pt_1P_1/C catalysts, the average sizes of the Pt and PtP particles in the Pt/C and Pt_1P_1/C catalysts are 3.1 and 3.5 nm, respectively. They are similar to that obtained from the above XRD measurement.

Fig. 4 shows the XPS spectrum of the Pt_1P_1/C catalyst in the Pt4*f* region. Pt4*f* peak of the Pt_1P_1/C catalyst can be fitted to two pairs of peaks. $Pt4f_{7/2}$ peak at 71.5 eV and $Pt4f_{5/2}$ peak at 74.9 eV are assigned to Pt^0, while $Pt4f_{7/2}$ peak at 72.6 eV and $Pt4f_{5/2}$ peak at 76.0 eV are assigned to Pt^{II}. $Pt4f_{7/2}$ and $Pt4f_{5/2}$ peaks of Pt° in the Pt/C catalyst are located at 70.9 and 74.3 eV, respectively [25].

3.2. Measurements of electrocatalytic performance of Catalysts

Fig. 5 displays the linear sweeping voltammograms of oxygen saturated in 0.5 M H_2SO_4 solution at the different catalysts. The onset potentials of ORR at the Pt_8P_1/C, Pt_4P_1/C, Pt_2P_1/C, Pt_1P_1/C, Pt_1P_2/C and Pt/C catalysts are 0.75, 0.73, 0.75, 0.79, 0.68 and 0.66 V, respectively. The limiting current densities (i_L) of ORR are 5.60, 6.15, 5.63, 5.77, 6.83 and 5.20 $mA\,cm^{-2}$, respectively. According to the treatment method in Ref. [26], the kinetic current densities (i_K) of ORR were calculated. As shown in Fig. 6, i_K at 0.65 V of the Pt_8P_1/C, Pt_4P_1/C, Pt_2P_1/C, Pt_1P_1/C, Pt_1P_2/C and Pt/C catalysts are 1.29, 0.95, 1.25, 1.66, 0.41, 0.32 $mA\,cm^{-2}$, respectively. The onset potentials of oxygen reduction at all the PtP/C catalysts are more positive than that at the Pt/C catalyst and i_K at all the PtP/C catalysts are larger than that at the Pt/C catalyst. For example, the onset potential of oxygen reduction at the Pt_1P_1/C catalyst is 0.13 V more positive than that at the Pt/C catalyst and i_K at the Pt_1P_1/C catalyst is 1.34 $mA\,cm^{-2}$ larger than that at the Pt/C catalyst.

4. Discussion

The result of EDX measurement of the Pt_1P_1/C catalyst (Fig. 1) indicates that the weight ratio of Pt and P in the Pt_1P_1/C catalyst is about 4:1, illustrating that the content of P in the Pt_1P_1/C catalysts prepared with this phosphorus yellow reduction method are much